

# Structural, optical and thermal characteristics of a novel orthorhombic L-proline thiourea monohydrate

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Received: 21 July 2011 / Accepted: 29 September 2011 / Published online: 22 October 2011  
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**Abstract** Single crystals of  $[(C_5H_9NO_2)(CH_4N_2S)] \cdot H_2O$ , L-proline thiourea monohydrate (LPTU), were grown by slow evaporation technique at room temperature. LPTU crystallizes in the zwitter ionic form with carboxyl group deprotonated and amino group protonated. An X-ray structure analysis yielded space group  $P_{212121}$ ,  $a = 5.769$  (3) Å,  $b = 10.074$  (4) Å,  $c = 17.438$  (9) Å,  $z = 4$  and  $\rho = 1.372$  mg/m<sup>3</sup> at 293 K. Neighbouring cations and anions are connected by hydrogen bonds to each other and also to water molecule. The dihedral angle between thiourea and water molecule is 86.76°. The pyrrolidine ring adopts a *twisted* conformation. The second harmonic generation test and the thermal stability of the crystal were investigated.

**Keywords** Slow evaporation technique · Crystal structure · Intra and inter molecular bonding · Second harmonic generation · Thermal stability

## Introduction

Non-linear optical (NLO) materials are highly sought over for the last three decades because of their efficient applications in many fields such as optical telecommunication,

optical computing, optical data storage and optical information processing [1]. Organic NLO single crystals possess the advantage of flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high non-linearity, high damage threshold, etc. The origin of non-linearity in NLO materials arises due to the presence of delocalized  $\pi$  electrons. Many natural amino acids individually exhibit the NLO properties [2] because they have a donor  $NH_2$  and acceptor  $COOH$  and also intermolecular charge transfer is possible. Proline is an abundant amino acid in collagen and is exceptional among the amino acids because it is the only one in which the amine group is part of a pyrrolidine ring making it rigid and directional in biological systems [3]. L-Proline single crystals show no centre of symmetry [4] and structures of L-proline monohydrate [5], DL-proline monohydrate [6], DL-proline hydrochloride [7], L-prolinium picrate and 2-methyl pyridinium picrate [8], the salt of L-prolinium picrate [9] have been reported. Crystal structure analysis of L-proline thiourea monohydrate (LPTU) grown by slow evaporation technique at room temperature is reported in this article. Second harmonic generation (SHG) test and the thermal studies augmented the capability of the crystal as potential NLO material for a commendable temperature range.

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## Experimental

L-proline thiourea monohydrate was synthesized by dissolving L-proline and thiourea in 1:1 equimolar ratio in Millipore water at room temperature. Good optical quality crystals of LPTU were harvested after a period of 50–60 days. Single crystal X-ray diffraction data for the structure analysis were collected at room temperature using

**Table 1** Crystal data and structure refinement

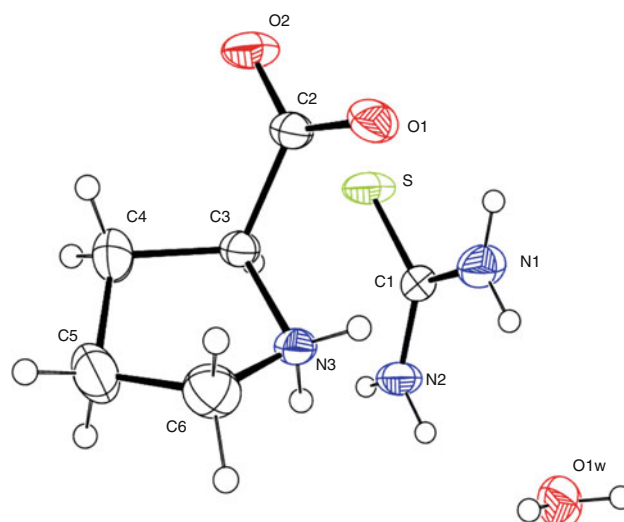
CCDC no.	808372
Empirical formula	[(C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub> )(CH <sub>4</sub> N <sub>2</sub> S)]·H <sub>2</sub> O
Formula weight	209.27
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	$a = 5.7689(3)$ Å, $\alpha = 90^\circ$ $b = 10.0738(4)$ Å, $\beta = 90^\circ$ $c = 17.4382(9)$ Å, $\gamma = 90^\circ$
Volume	1013.42(8) Å <sup>3</sup>
Z, calculated density	4, 1.372 mg/m <sup>3</sup>
Absorption coefficient	0.303 mm <sup>-1</sup>
$F(000)$	448
Crystal size	0.30 × 0.25 × 0.20 mm
$\theta$ range for data collection	2.33°–31.91°
Limiting indices	$-5 \leq h \leq 8$ , $-14 \leq k \leq 7$ , $-24 \leq l \leq 25$
Reflections collected/unique	8063/3451 [ $R(\text{int}) = 0.0225$ ]
Completeness to $\theta = 31.91^\circ$	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9420 and 0.9147
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3451/4/154
Goodness-of-fit on $F^2$	1.031
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0399$ , $wR2 = 0.0972$
$R$ indices (all data)	$R1 = 0.0582$ , $wR2 = 0.1061$
Absolute structure parameter	0.00(7)
Largest diff. peak and hole	0.300 and $-0.173$ e.Å <sup>-3</sup>

Bruker Kappa Apex 2 CCD diffractometer with MoK $\alpha$  radiation. Crystal Structure was solved by direct method using the program SHELXS97 [10] and refined on  $F^2$  by full-matrix least-squares procedures to a reliability value of 4.0%. All the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C–H = 0.97 Å for methylene H and with  $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C})$ . The positions of other hydrogen atoms were located from difference Fourier maps and they were allowed to ride on the corresponding non-hydrogen atoms with  $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C}, \text{N})$  and  $\text{Uiso}(\text{H}) = 1.5\text{Ueq}(\text{O})$ . Bond distances N1–H1A, N1–H1B, N2–H2A and N2–H2B were restrained to 0.86 (1) Å. SHG test was performed using Nd:YAG laser. Thermal stability of the crystal was investigated by Thermo Gravimetric Analysis and Differential Thermal Analysis carried on NETZSCH STA 409C/CD in Nitrogen

**Table 2** Atomic coordinates and temperature factors

Atoms	$x$	$y$	$z$	U(eq)
C(1)	308(3)	10005(2)	3291(1)	32(1)
C(2)	−3421(3)	9413(2)	1392(1)	32(1)
C(3)	−1138(2)	10129(1)	1242(1)	30(1)
C(4)	−1272(3)	11047(2)	542(1)	48(1)
C(5)	849(4)	10715(2)	68(1)	54(1)
C(6)	1227(4)	9262(2)	222(1)	49(1)
N(1)	−114(3)	8764(2)	3070(1)	50(1)
N(2)	2477(2)	10416(2)	3275(1)	43(1)
N(3)	758(2)	9170(1)	1056(1)	33(1)
O(1)	−3481(2)	8190(1)	1343(1)	49(1)
O(2)	−5097(2)	10148(1)	1558(1)	46(1)
O(1W)	4902(3)	7735(1)	2934(1)	50(1)
S	−1857(1)	11022(1)	3570(1)	51(1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

**Fig. 1** Ortep plot of the molecule drawn at 30% probability

atmosphere in the temperature range of 25–900 °C with a heating rate of 10 K/min. TG-DTA and optical studies are very important methods for materials characterization. Therefore, many authors have used these methods for investigation of various materials [11–25].

## Results and discussion

### Crystal structure of orthorhombic LPTU

The title molecule consists of a proline, thiourea and a water molecule. The angle between the plane of carboxyl group and the pyrrolidine ring is 57.90°. The thiourea and the water molecule are nearly perpendicular to each other

**Table 3** Selected bond lengths/Å for non-hydrogen atoms

Atoms	Distances
C(1)–N(2)	1.319(2)
C(1)–N(1)	1.330(2)
C(1)–S	1.687(2)
C(2)–O(1)	1.236(2)
C(2)–O(2)	1.252(2)
C(2)–C(3)	1.524(2)
C(3)–N(3)	1.495(2)
C(3)–C(4)	1.533(2)
C(4)–C(5)	1.513(3)
C(5)–C(6)	1.505(3)
C(6)–N(3)	1.482(2)

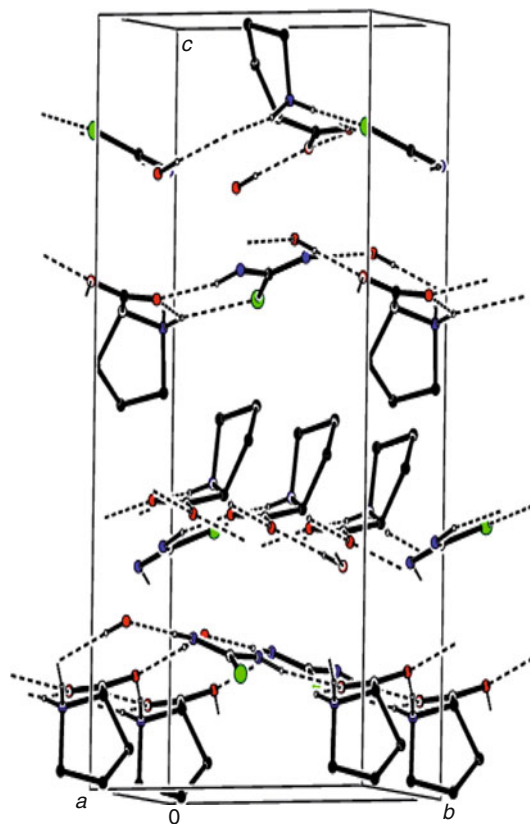
**Table 4** Selected bond angles/° for non-hydrogen atoms

Atoms	Angles
N(2)–C(1)–N(1)	117.6(2)
N(2)–C(1)–S	121.1(1)
N(1)–C(1)–S	121.3(1)
O(1)–C(2)–O(2)	125.8(1)
O(1)–C(2)–C(3)	118.9(1)
O(2)–C(2)–C(3)	115.3(1)
N(3)–C(3)–C(2)	111.4(1)
N(3)–C(3)–C(4)	104.7(1)
C(2)–C(3)–C(4)	112.3(1)
C(5)–C(4)–C(3)	105.1(2)
C(6)–C(5)–C(4)	103.6(2)
N(3)–C(6)–C(5)	102.0(2)

**Table 5** Selected torsion angles/° for non-hydrogen atoms

Atoms	Angles
O(1)–C(2)–C(3)–C(4)	116.5(2)
O(2)–C(2)–C(3)–C(4)	–63.5(2)
C(2)–C(3)–C(4)–C(5)	–131.3(2)
C(3)–C(4)–C(5)–C(6)	31.9(2)
C(4)–C(5)–C(6)–N(3)	–40.9(2)
C(5)–C(6)–N(3)–C(3)	35.3(2)
C(2)–C(3)–N(3)–C(6)	106.0(2)
C(4)–C(3)–N(3)–C(6)	–15.6(2)

and are oriented at an angle of 86.76° with respect to each other. The pyrrolidine ring N3/C3–C6 adopts a *twisted* conformation with puckering parameters [26] of  $Q_2 = 0.393(2) \text{ \AA}$ ,  $\varphi_2 = 309.0(3)^\circ$  and asymmetry parameters [27] of  $\Delta C_5(C6) = 0.080(1)$ ,  $\Delta C_2(C3) = 0.013(1)$ . Atom

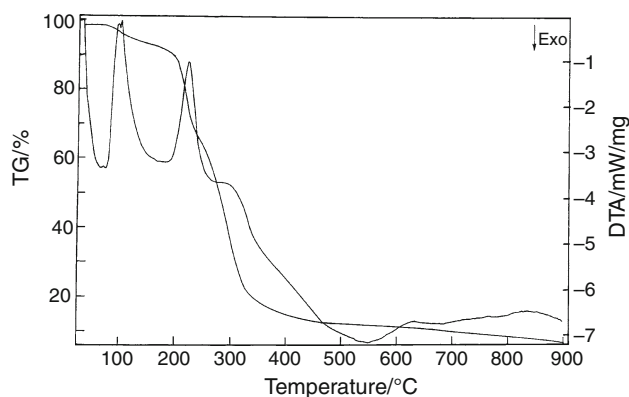
**Fig. 2** Packing diagram of the molecule viewed down *a* axis**Table 6** Possible hydrogen bonds/Å/°

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1A)...O(1W)#1	0.86(9)	2.21(10)	3.066(2)	179(2)
O(1W)–H(1C)...O(1)#2	0.86(4)	2.24(4)	2.96(2)	142(3)
O(1W)–H(1D)...O(2)#3	0.77(3)	1.99(3)	2.754(19)	172(3)
N(2)–H(2A)...O(1)#4	0.85(10)	2.09(11)	2.930(2)	169(2)
N(3)–H(3A)...O(2)#2	0.87(2)	1.88(2)	2.731(18)	164(19)

Symmetry codes: #1:  $x - 1, y, z$ ; #2:  $x + 1, y, z$ ; #3:  $-x, y - 1/2, -z + 1/2$ ; #4:  $-x, y + 1/2, -z + 1/2$

N1 deviates by 0.543(2) Å from the least-squares plane through the remaining four atoms. The crystal structure is stabilized by a three-dimensional network of N–H...O and O–H...O hydrogen bonds. Intramolecular hydrogen bonding was observed between O1W of water molecule and O2 of carboxyl group and also between N3 of amino group and S of thiourea. The hydrogens (N1H1B and N2H2B) of thiourea are bonded to water molecule oxygen O1W by intermolecular interactions. In addition, the hydrogen (O1WH1C) is also bonded to carboxylate oxygen O1 by intermolecular bondings.

The crystal data and details of the structure determination and refinement are given in Table 1. The atomic



**Fig. 3** TG/DTA curve of LPTU crystal

coordinates and temperature factors for the non-hydrogen atoms are given in Table 2. The ORTEP plot of the molecule is shown in Fig. 1. Selected bond lengths, bond angles and torsion angles are given in Tables 3, 4 and 5 respectively. The three-dimensional packing of molecules viewed down *a* axis is shown in Fig. 2.

The molecules are linked through intra (N–H···O) and inter molecular bonding which generates edge fused  $R_2^2$  (6) ring motif. The Hydrogen bonded motif are linked to each other to form a three-dimensional network. It seems to be effective in the stabilization of crystal structure to form chains [28]. There are five polar hydrogen atoms on the fragment, one on N1, one on N2, two on N3 and one on H1D of water molecule participating in the hydrogen bond. The dimensions of the hydrogen bond are listed in Table 6. The conformation of the fragment is such that the nitrogen, sulphur atom of the thiourea unit and oxygen, nitrogen atom of proline unit is oriented in such a way to form inter and intra molecular hydrogen bond resulting in the formation of a ring.

#### Second harmonic generation

In the SHG test [29], LPTU crystal was illuminated by a Nd:YAG laser of 1064 nm with a pulse width of 8 ns, the emission of green radiation from the sample confirmed the SHG and the lattice to be noncentric.

#### Thermal studies

Thermogravimetric analysis (TG) of the crystal was carried out using NETSCH STA 409C/CD in the range of 25–900 °C with a heating rate of 10 K/min in nitrogen atmosphere. Alumina was taken as the reference material in an Al<sub>2</sub>O<sub>3</sub> crucible. The initial mass loss of 5.2% between 80 and 140 °C is due to loss of water from the crystal lattice [30]. The second mass loss of 28% between 200 and 240 °C is due to the loss of (–CS–NH) unit of thiourea. The

final major mass loss of 53% that occurs between 240 and 460 °C is assigned to the degradation of L-proline.

In the differential thermal analysis (DTA), the endotherm lying between 80 and 140 °C is assigned to the loss of water from the crystal lattice. It is also matching with the mass loss in TG trace. The second endotherm lying between 200 and 250 °C is due to the loss of a unit of thiourea. It is also matching with mass loss in TG. The third endotherm between 250 and 460 °C is due to degradation of L-proline and it could be concluded that the material degrades without melting. Figure 3 shows the combined TG and DTA curve.

#### Conclusions

A novel NLO material was synthesized by slow evaporation technique. The crystal structure is stabilized by a three-dimensional network of N–H···O and O–H···O hydrogen bonds. The conformation of the crystal is due to the intra and inter molecular bonding which generate edge fused  $R_2^2$  (6) ring. SHG test confirms the noncentric lattice of the crystal. The thermal stability of the crystal goes up to 100 °C which makes it a potential candidate for NLO applications in that temperature range.

**Acknowledgements** The authors thank Dr. Babu Varghese, SAIF, IIT, Chennai, Prof. P.K. Das, IPC, IISc., Bangalore and Dr. K. Kartikeyan, Department of Chemistry, Sathyabama University, Chennai for their help and support rendered.

Supporting Information Available: CCDC 808372 is the deposition number for the crystal data deposited at Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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